Structure of the Aluminotitanium Hydride $[(C_5H_5)(C_5H_4)TiHAl(C_2H_5)_2]_2$

By FRED N. TEBBE* and LLOYD J. GUGGENBERGER

(*Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware* 19898)

Summary A model olefin polymerization catalyst characterized in the past as $[(C_5H_5)_2TiAlEt_2]_2$ is shown to be a hydride complex $[(C_5H_5)(C_5H_4)TiHAlEt_2]_2$, with the hydride ligand presumably bridging the titanium and aluminium atoms.

$$\left.\begin{array}{ll}(1) & (C_5H_5)_2TiPh_2 \\ (2) & (C_5H_5)_2TiCl_2 \\ (3) & (C_5H_5)_2TiCl\end{array}\right\} \xrightarrow{Et_3Al} \underset{(\mathbf{1})}{[(C_5H_5)(C_5H_4)TiHAlEt_2]_2}$$

THE reactions expressed by equations (1)—(3) produce the dimeric aluminotitanium hydride (**1**). The product is structurally related to a new class of μ-(1—5-η:σ-C_5H_4)-(1—5-η-C_5H_5) transition-metal complexes established by studies of $[(C_5H_5)(C_5H_4)NbH]_2$[1a–c] and $(C_5H_5)(CO)MoC_5H_4Mn(CO)_4$,[1d] and is the first well-characterized member of a series of dimeric titanium–aluminiumalkyl hydrides. We have shown that (**1**) is identical to a material previously synthesized by reaction (3) and incorrectly characterized as $[(C_5H_5)_2TiAlEt_2]_2$.[2]

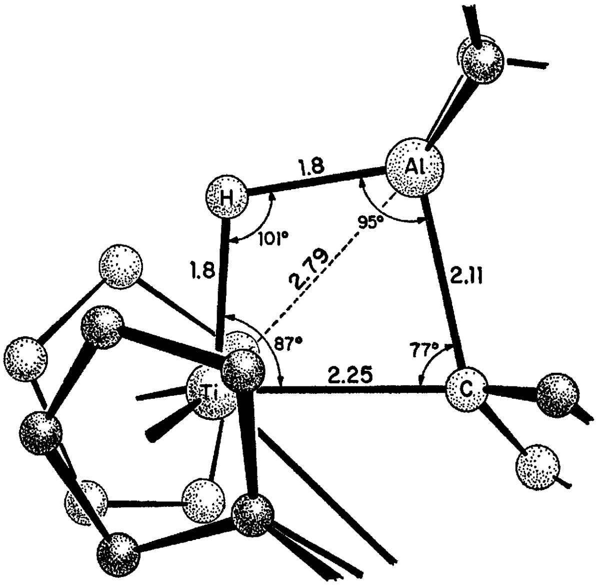

FIGURE 1. *Suggested hydride geometry for* $[(C_5H_5)(C_5H_4)TiHAlEt_2]_2$ *(distance and angles involving the hydride atom result from an assumed position).*

The products obtained by the new routes (1) and (2) were equivalent to one another,† and to the material we obtained following the reported procedure [equation (3)].[2b] The conditions for reactions (1) and (2) were the same. In (1), a mixture of 5·0 g (0·015 mol) of $(C_5H_5)_2TiPh_2$,[4] 6·9 g (0·060 mol) of Et_3Al, and 30 ml of benzene was agitated at 70° for 12 h in a stainless steel pressure vessel to produce a gas, primarily ethane, and 2·7 g of (**1**). Single crystals of (**1**) were grown from n-heptane solutions.

The ^1H n.m.r. spectrum consists of resonances from C_5H_5 at τ 4·92; C_5H_4 at 3·14, 4·17, 5·07, and 5·71; CH_3CH_2 at 8·54 and 8·68; CH_3CH_2 at 9·36 and 9·54; and metal hydride at 17·02. The n.m.r., m.s., molecular weight, and analytical data define the composition as $[(C_5H_5)(C_5H_4)TiHAlEt_2]_2$ and suggest a framework structure based on that of $[(C_5H_5)(C_5H_4)NbH]_2$.[1a–c] *X*-Ray studies on a crystal of (**1**) established its identity with "$[(C_5H_5)_2TiAlEt_2]_2$."[2a]

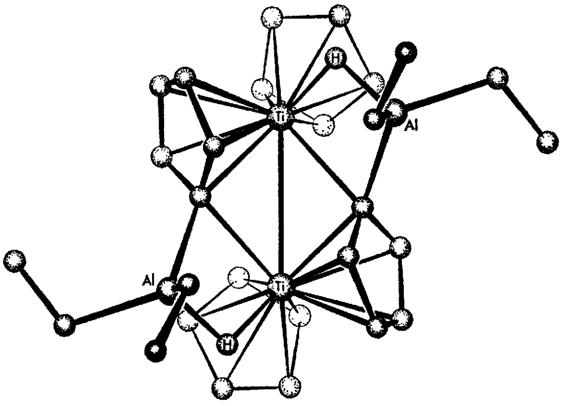

FIGURE 2. *Suggested structure for* $[(C_5H_5)(C_5H_4)TiHAlEt_2]_2$.

By examination of a model of the structure for "$[(C_5H_5)_2TiAlEt_2]_2$"[2a] we find the bridging cyclopentadienyl rings can accommodate only 4 hydrogens.‡ The n.m.r. spectrum shows that the hydrogens displaced from the rings are metal co-ordinated. We believe these hydrogens complete a tetrahedral geometry around the aluminium atoms by bridging the titanium and aluminium centres, as shown in Figures 1 and 2.

Compound (**1**) was characterized as a soluble, model olefin polymerization catalyst.[2b] It is significant that this catalyst is newly defined as a metal hydride complex.

(*Received*, 18*th January* 1973; *Com.* 071.)

---

† Reaction (2) was reported to yield $(C_5H_5)_2TiCl_2AlEt_2$.[3] Under our conditions (2) produced both the chloride complex and (**1**). The two compounds were separated by crystallization.

‡ Wailes and Weigold also recognized this problem and suggested reformulation of "$[(C_5H_5)_2TiAlEt_2]$" as $[(C_5H_5)(C_5H_4)TiAlEt_2]_2$ (**2**).[5] We have now repeated the Wailes and Weigold experiments and find that (**1**) and (**2**) are compositionally distinct species.

[1] (a) F. N. Tebbe and G. W. Parshall, *J. Amer. Chem. Soc.*, 1971, **93**, 3793; (b) L. J. Guggenberger and F. N. Tebbe, *ibid.*, p. 5924; (c) L. J. Guggenberger, *Inorg. Chem.*, 1973, in the press; (d) R. Hoxmeier, B. Deubzer, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1971, **93**, 536.

[2] (a) P. Corradini and A. Sirigu, *Inorg. Chem.*, 1967, **6**, 601; (b) G. Natta, G. Mazzanti, P. Corradini, U. Giannini and S. Cesca, *Atti Accad. naz. Lincei, Rend., Classe. Sci. fis. mat. nat.*, 1959, **26**, 150.

[3] G. Natta, P. Pino, G. Mazzanti, and U. Giannini, *J. Amer. Chem. Soc.*, 1957, **79**, 2975.

[4] L. Summers, R. H. Uloth, and A. Holmes, *J. Amer. Chem. Soc.*, 1955, **77**, 3604.

[5] P. C. Wailes and H. Weigold, *J. Organometallic Chem.*, 1970, **24**, 713.

Printed by W Heffer & Sons Ltd Cambridge England